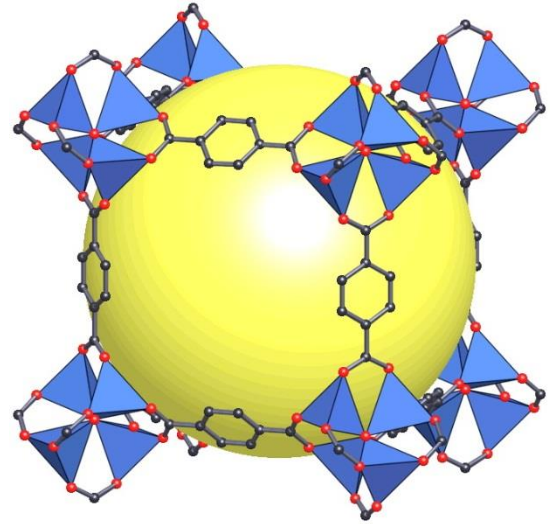
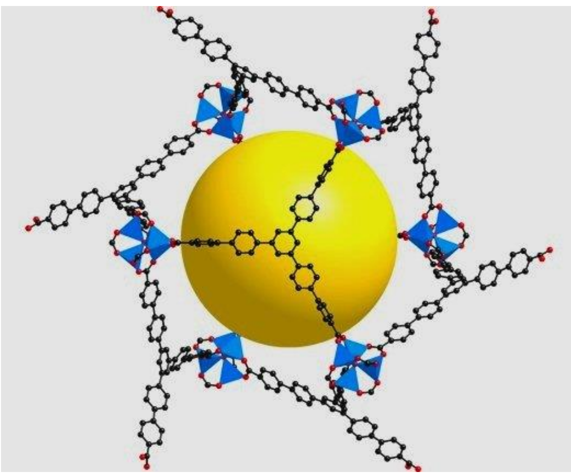
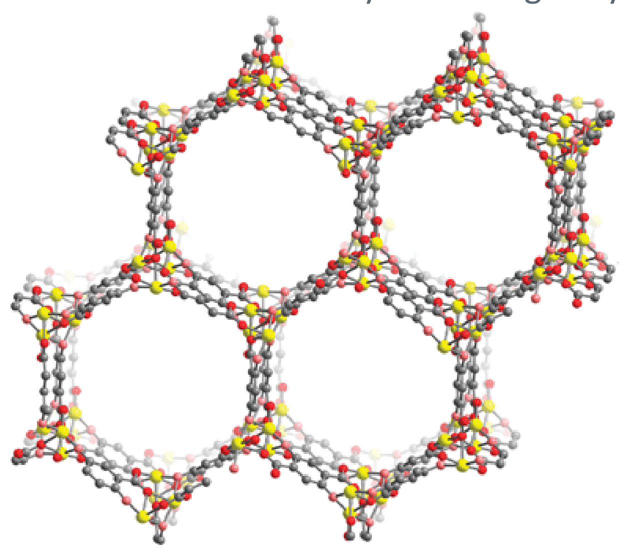




CO_2 Binding in Metal-Organic Frameworks

By: Tim Dougherty

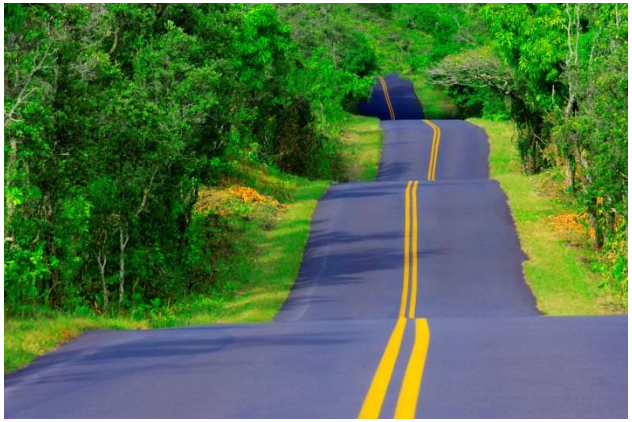


Qiu, S.; Zhu, G. Coordination Chemistry Reviews 2009, 253, 2891-2911.

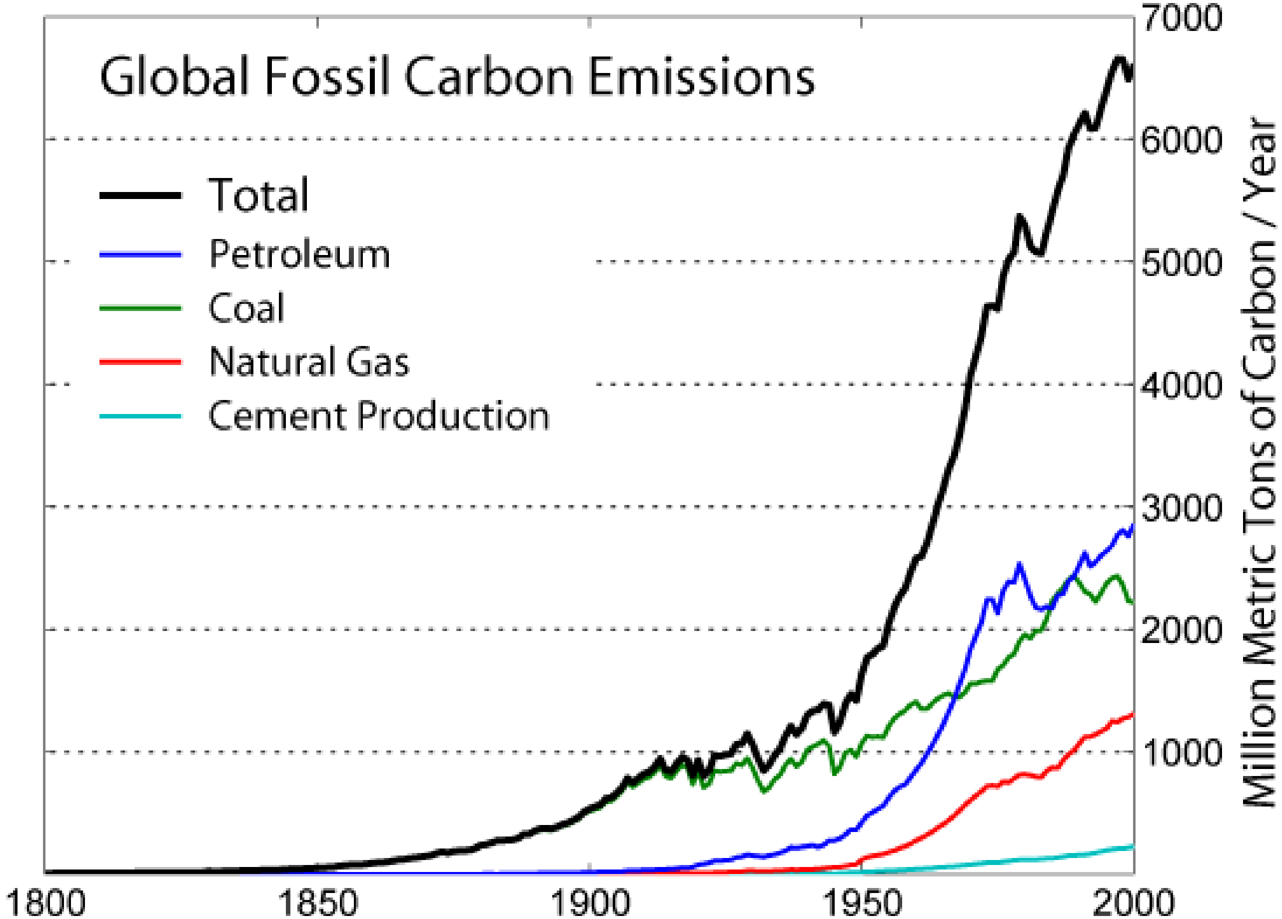
Rosi, N. L.; Eckert, J.; Eddoudi, M.; Vodak, D. T.; Kim, J.; O'Keefe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127.

Road Map: Where we're headed

- **Background**
- **Applications**
- **Current work** at NIST
- **Future work** after SURF

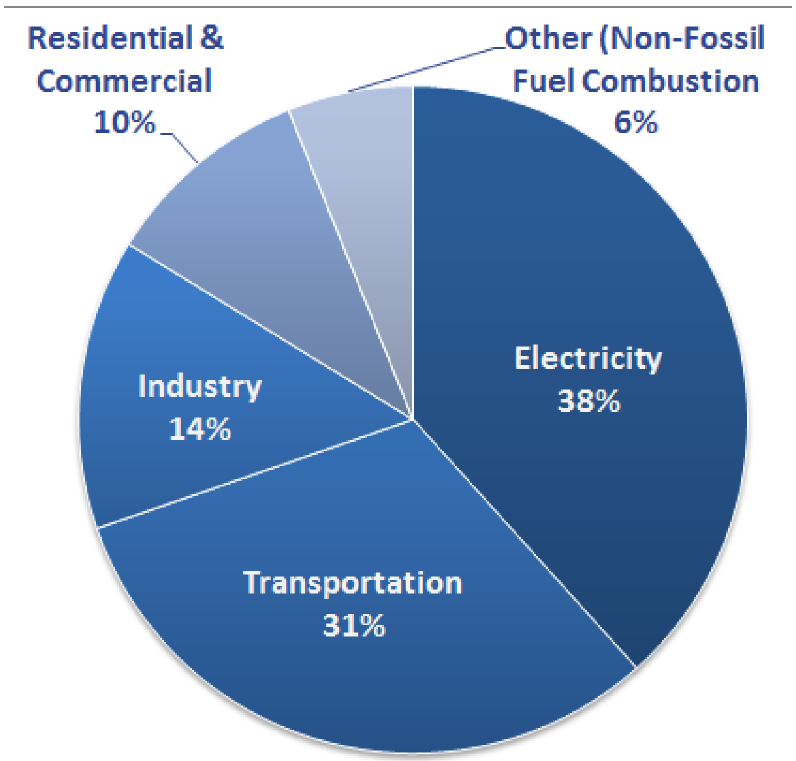


Today's CO_2 Problem



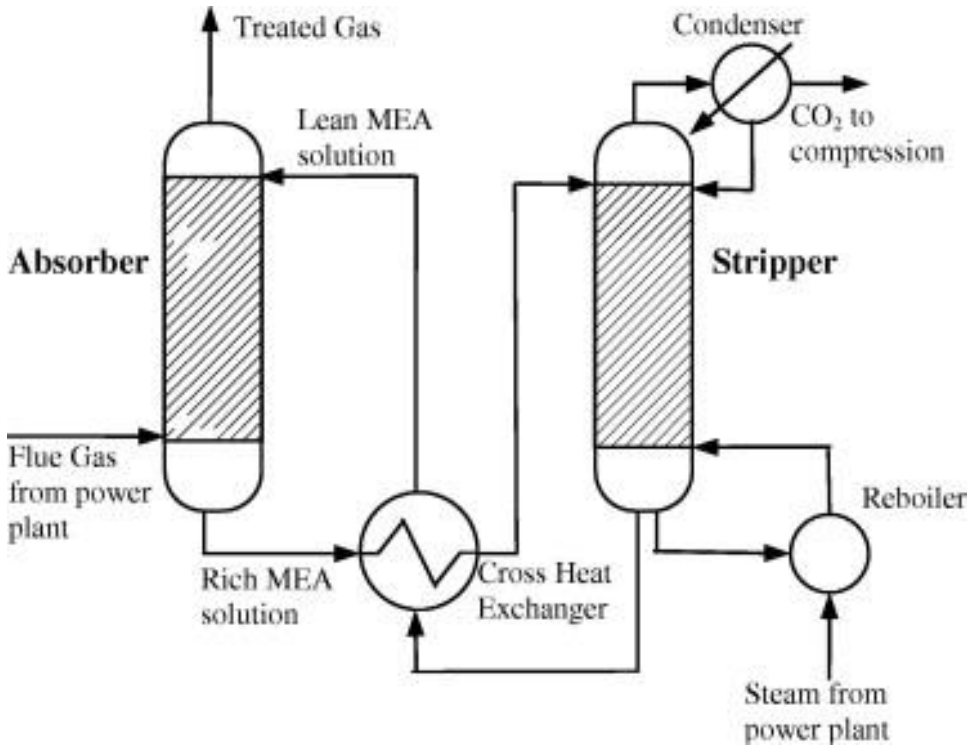
http://commons.wikimedia.org

Today's CO_2 Problem



http://www.epa.gov/climatechange/ghgemissions/gases/co2.html

Current Industrial Capture of CO_2 – Monoethanolamine (MEA) absorption



Commercial CO_2 Applications:

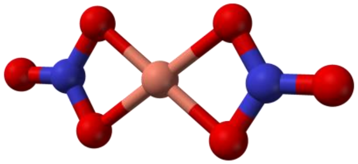
- Dry ice production
- Carbonation of beverages
- Urea production

- High cost in energy and capital
    - MEA reduces efficiency by 30%
- MEA is also toxic
- More efficient, less costly process are being developed
    - MOFs?

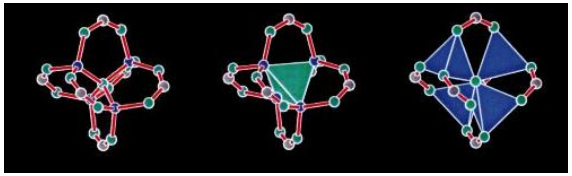
$$C_2H_4OHNH_2 + H_2O + CO_2 \leftrightarrow C_2H_4OHNH_3^+ + HCO_3^-$$

Lawal, A.; Wang, M.; Stephenson, P.; Yeung, H. *Fuel* **2009**, *88*, 2455-2462.
Herzog, H.; Golomb, D. *Encyclopedia of Energy* **2004**, *1*, 1-11.

What exactly is a metal organic framework?

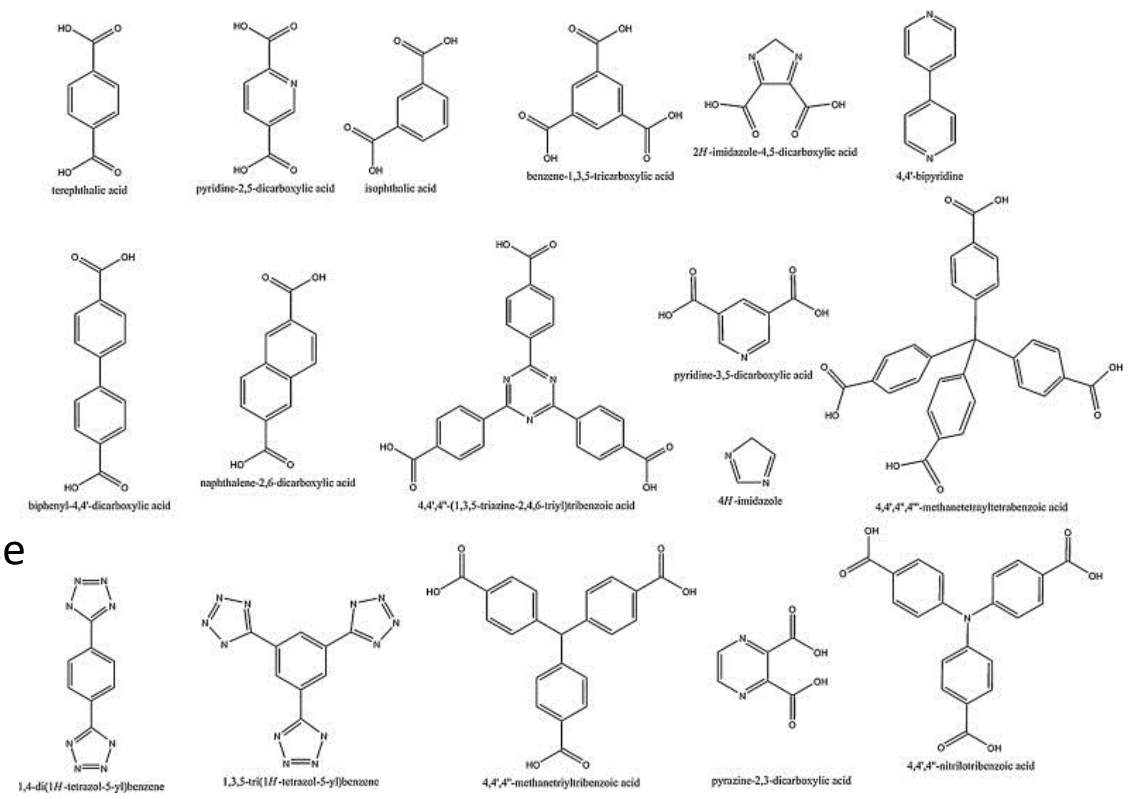


Cationic metal



Cationic metal cluster

+



Organic Linkers

- MOFs are metal cations or clusters connected through organic ligands to form rigid 3-D, often **porous**, structures
- Structure allows for much diversity among MOFs (synthetic precursors not constrained to those illustrated here)
- Synthetic make-up gives rise to diverse pore dimensionality, incredibly large surface areas, among other unique properties

Li, H.; Eddaoudi, M.; O'Keefe, M.; Yaghi, O. M. *Nature*, **1999**, *402*, 276-279.
Murray, L. J.; Dinca, M. Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294-1314.
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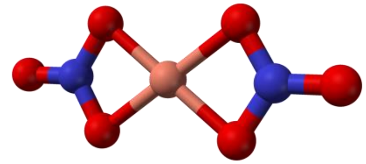

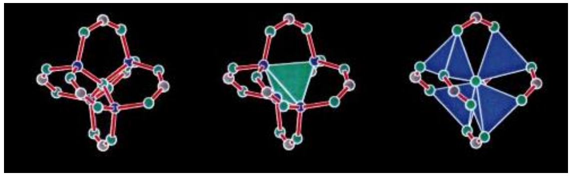

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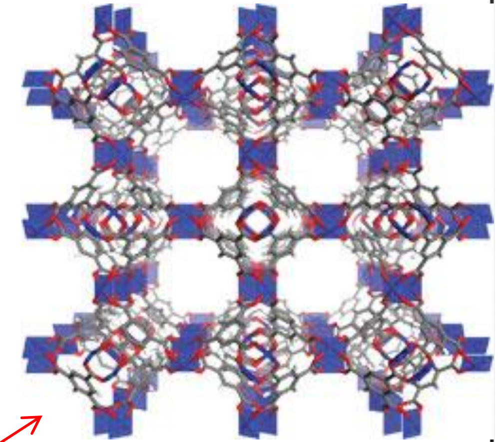

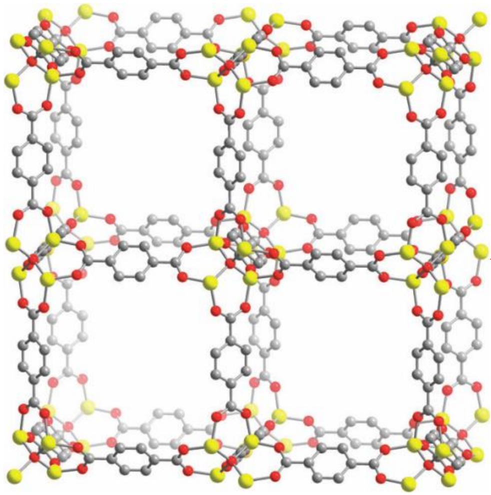

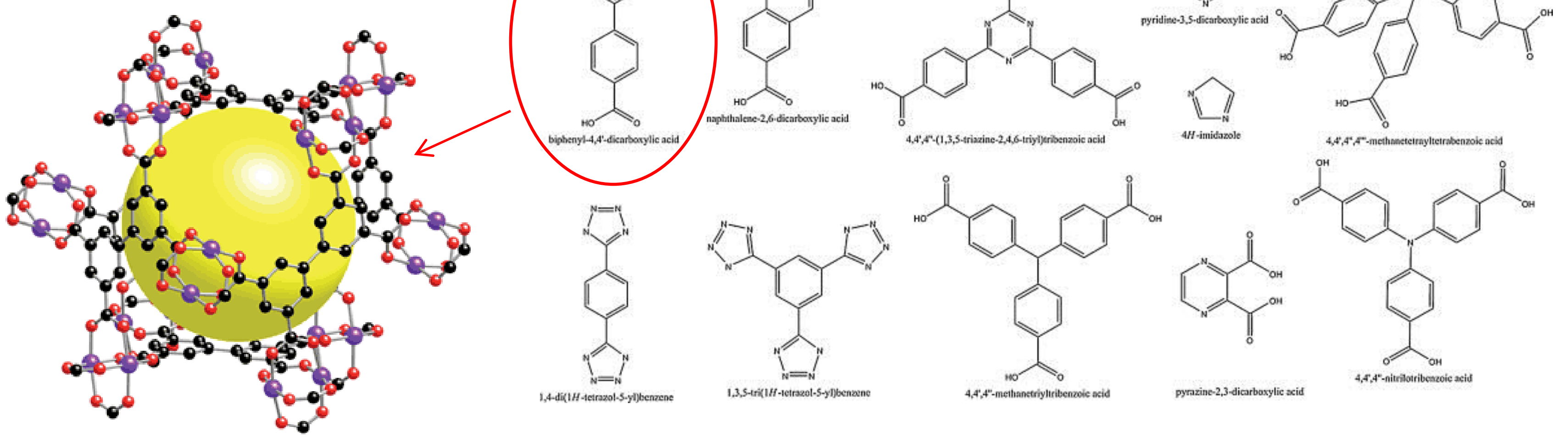

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Qiu, S.; Zhu, G. *Coordination Chemistry Reviews* **2009**, *253*, 2891-2911.

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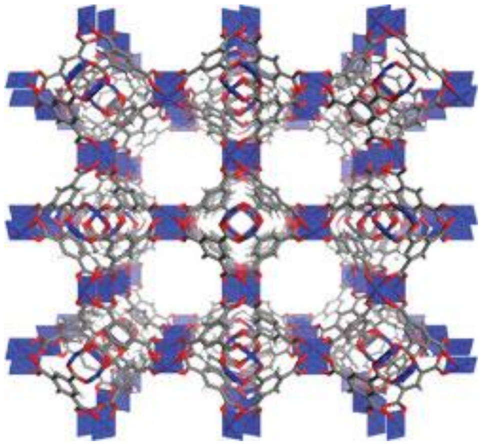
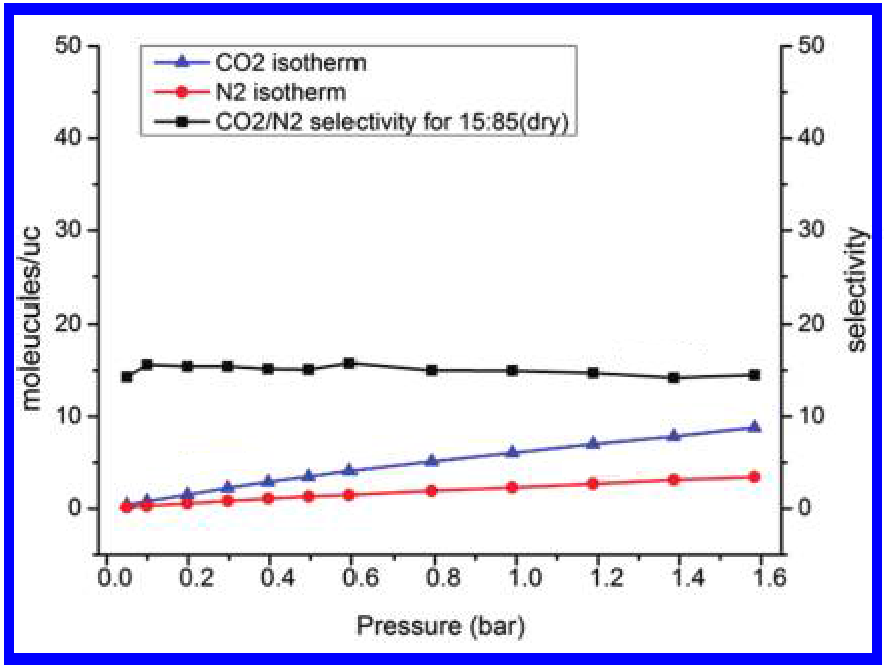
Applications of MOFs

- Catalysis
- H_2 storage
- Gas separations
  - Reversible CO_2 capture



MOF
$Cu_3(BTC)_2$



Yu, J.; Ma, Y.; Balbuena, P. B. *Langmuir* **2012**, *28*, 8064-8071.

Research at the NCNR

Synthesis and CO_2 adsorption study of the MOF family $M_3(BTC)_2$

Determination of CO_2 binding sites

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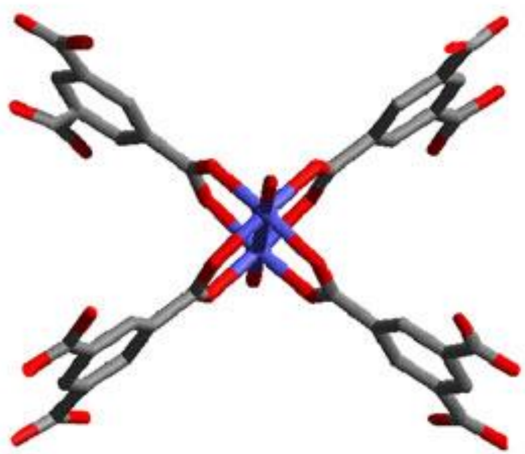
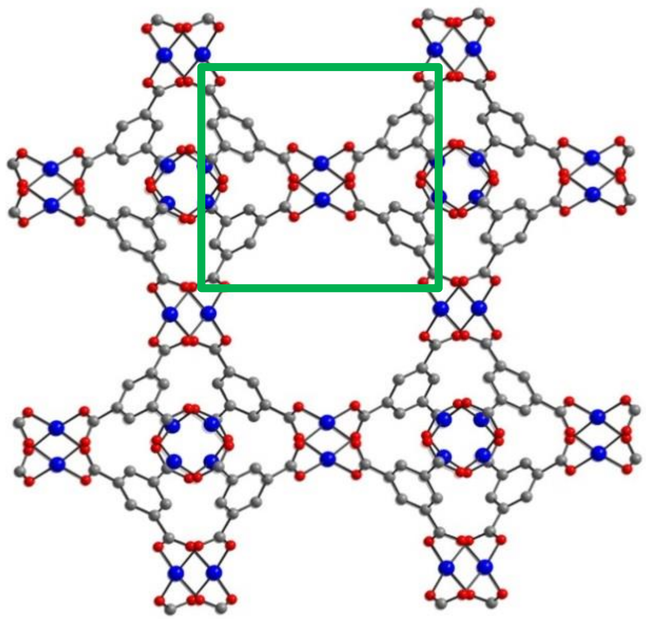
3-Dimensional Structure of $M_3(BTC)_2$

- As synthesized structure contains solvent molecules
- Solvent is easily removed upon heating
- Structural features attractive for gas adsorption:
    - 1 open metal site
    - 2 large channels or pores
    - 1 small pore

Oxygen – Red
Carbon – Gray
Metal – Blue





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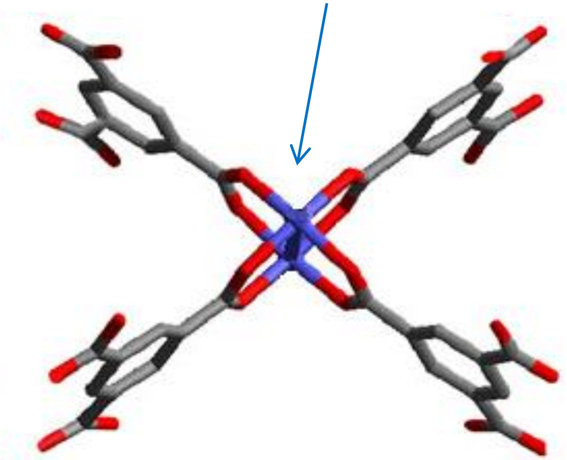
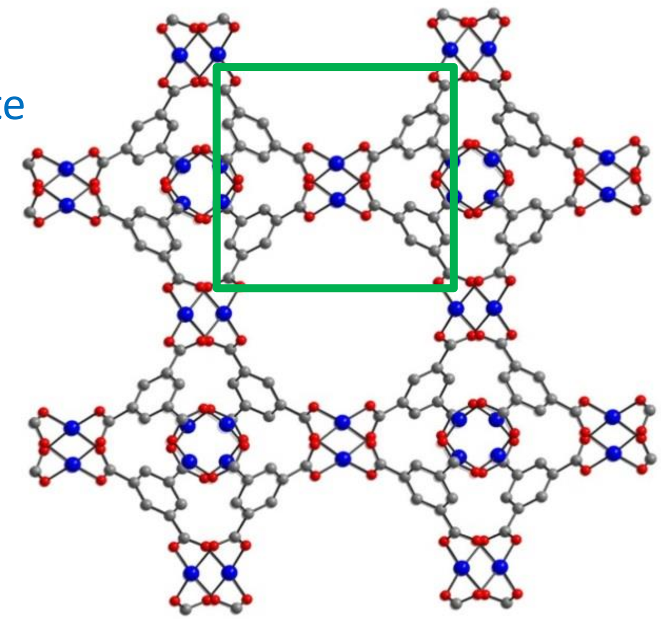
Coordinatively-
unsaturated metal site





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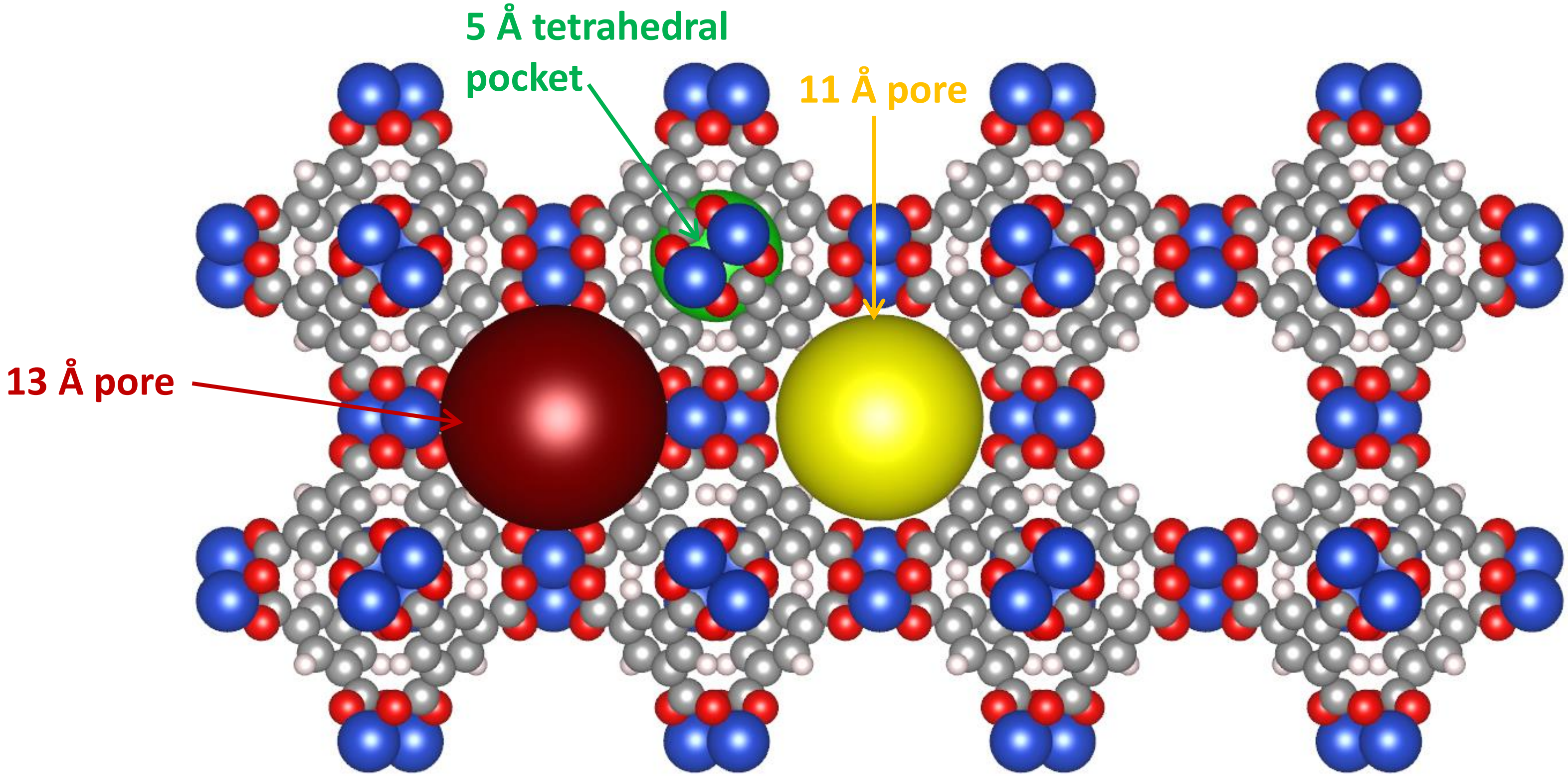

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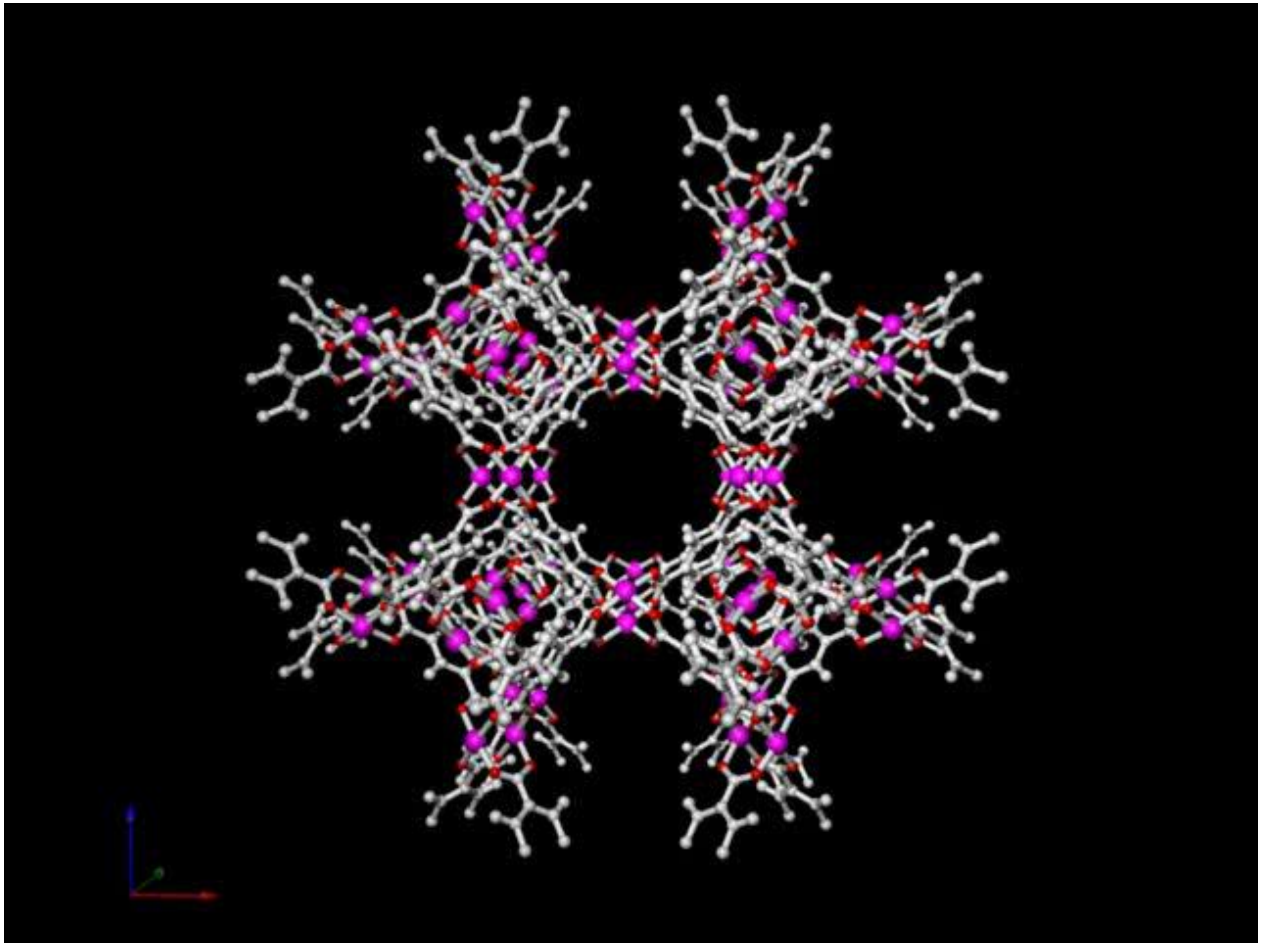
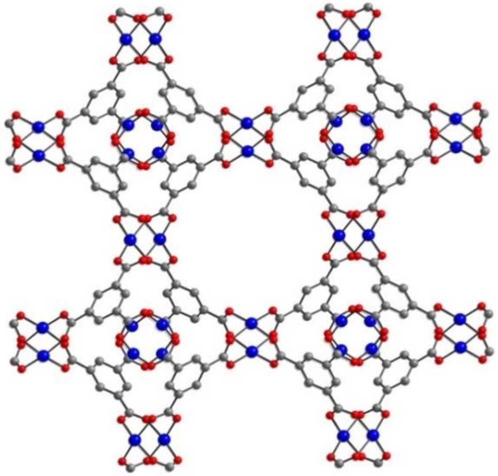
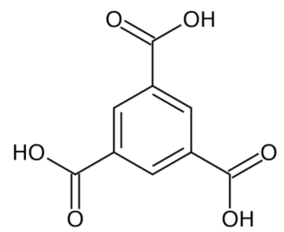


Synthesis

- $Cu_3(BTC)_2$
- $Cr_3(BTC)_2$ – air sensitive
- $Mo_3(BTC)_2$ – air sensitive (ongoing)



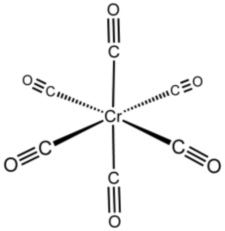
$Cu(NO_3)_2{\cdot}2.5H_2O$ +



$\xrightarrow[85^\circ C]{DMF:H_2O:EtOH}$ $Cu_3(BTC)_2$

Copper Nitrate Hemipentahydrate

Benzene-1,3,5-carboxylic acid (BTC)



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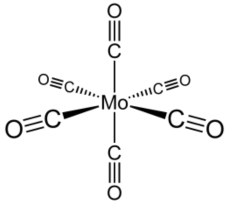

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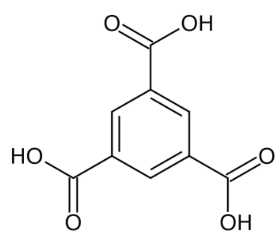

$\xrightarrow[155^\circ C]{DMF}$ $Cr_3(BTC)_2$ $Mo_3(BTC)_2$

Chromium/Molybdenum hexacarbonyl

Benzene-1,3,5-carboxylic acid (BTC)

Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148-50.
Wade, C. R.; Dinca, M. *Dalton Trans.* **2012**, *41*, 7931-7938.

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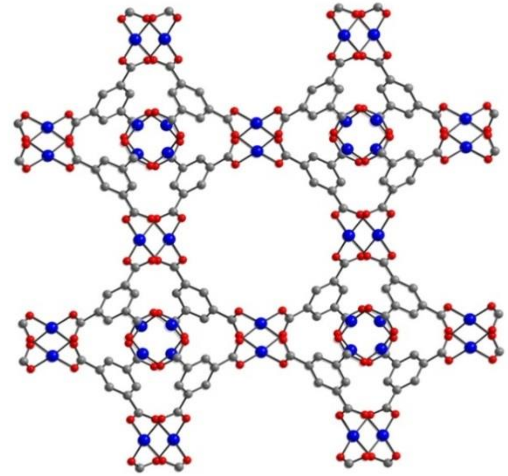
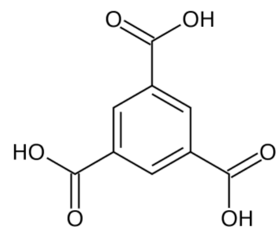


$Cu(NO_3)_2{\cdot}2.5H_2O$ + 

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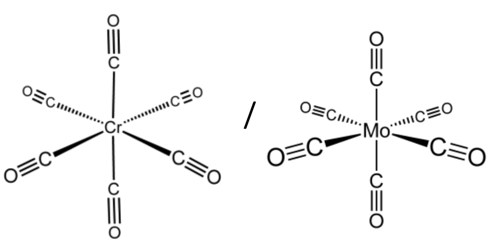
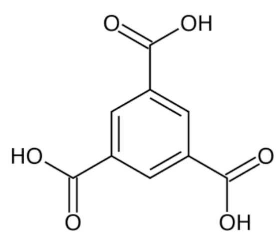


\+ 

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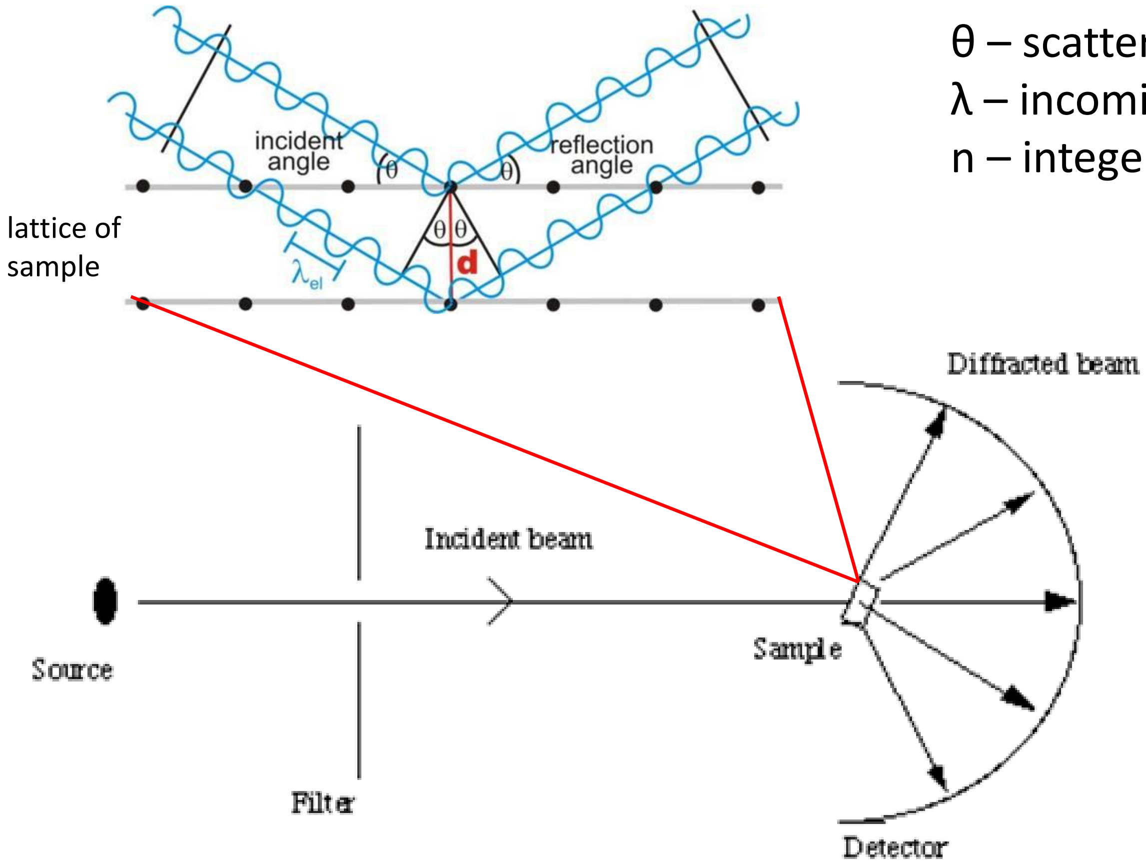
Wade, C. R.; Dinca, M. *Dalton Trans.* **2012**, *41*, 7931-7938.

Neutron Powder Diffraction



Bragg's Law:

$2d*\sin\theta = n\lambda$

d – lattice spacing

θ – scattering angle

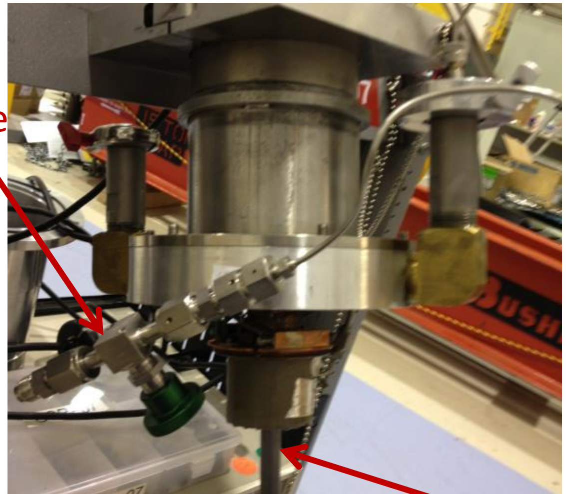
λ – incoming wavelength

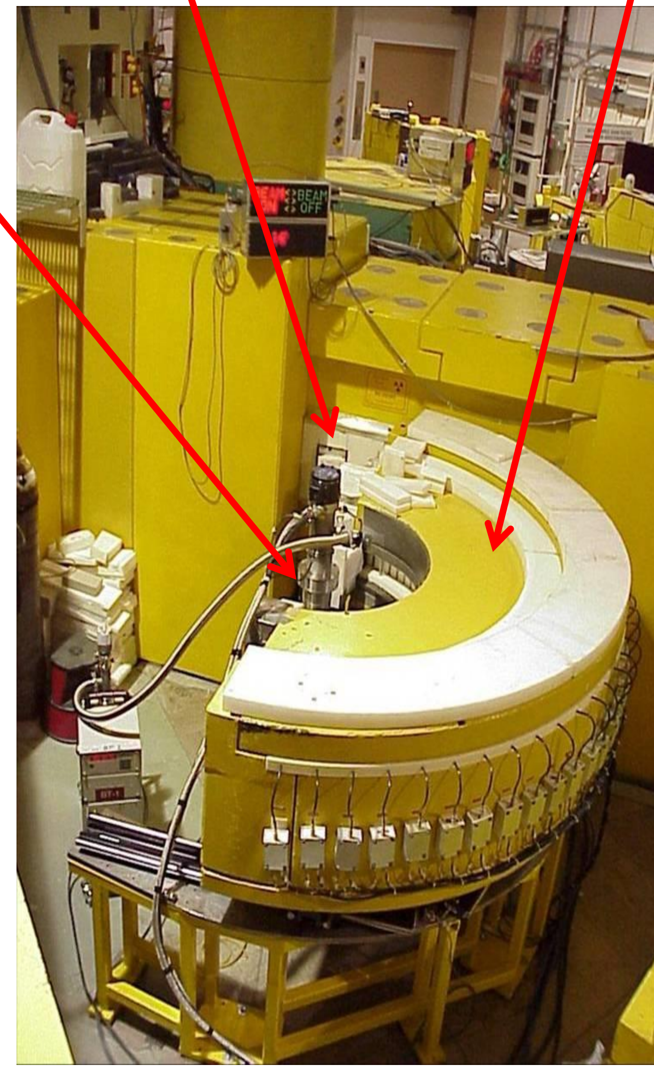
n – integer value

http://www.ncnr.nist.gov/instruments/bt1/

Prynn, R. *Neutron Scattering: A Primer*. Los Alamos Neutron Science Center.

Neutron Powder Diffraction



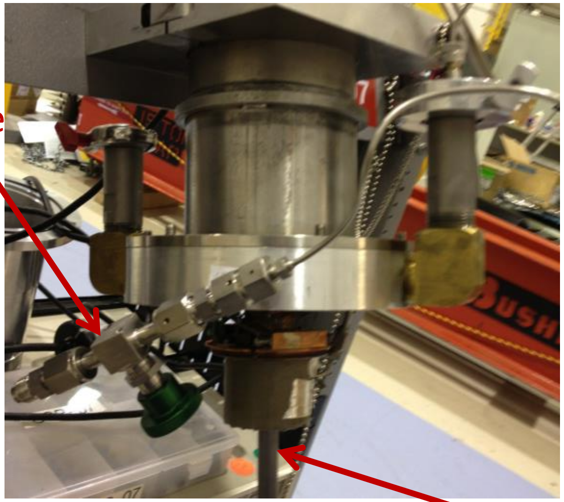


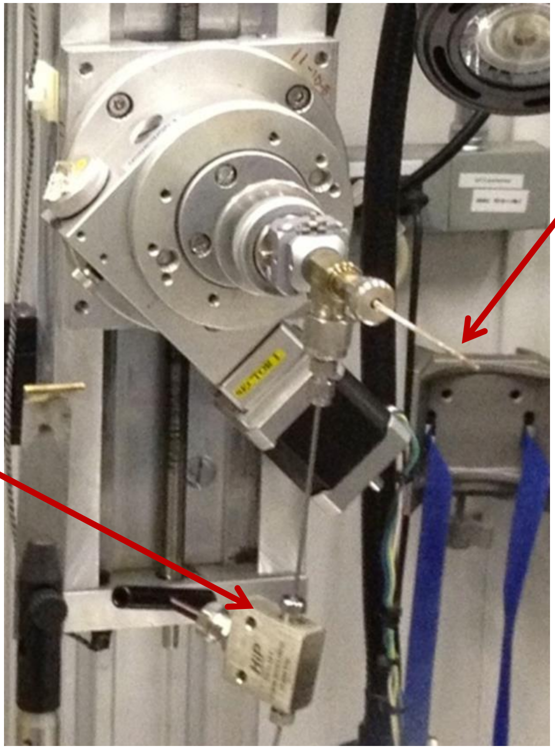
1.03 g $Cr_3(BTC)_2$ dosed at 6.12 bar CO_2 (1.5 CO_2 per Cr)
3.40 g $Cu_3(BTC)_2$ dosed at 30.98 bar CO_2 (2.5 CO_2 per Cu)

Benefits over X-ray Powder Diffraction:

- Gives accurate information about atomic positions due to availability of high scattering angles
- Allows easier **quantitative** analysis for gas dosing studies than XRPD

Neutron Powder Diffraction





X-ray powder diffraction set-up

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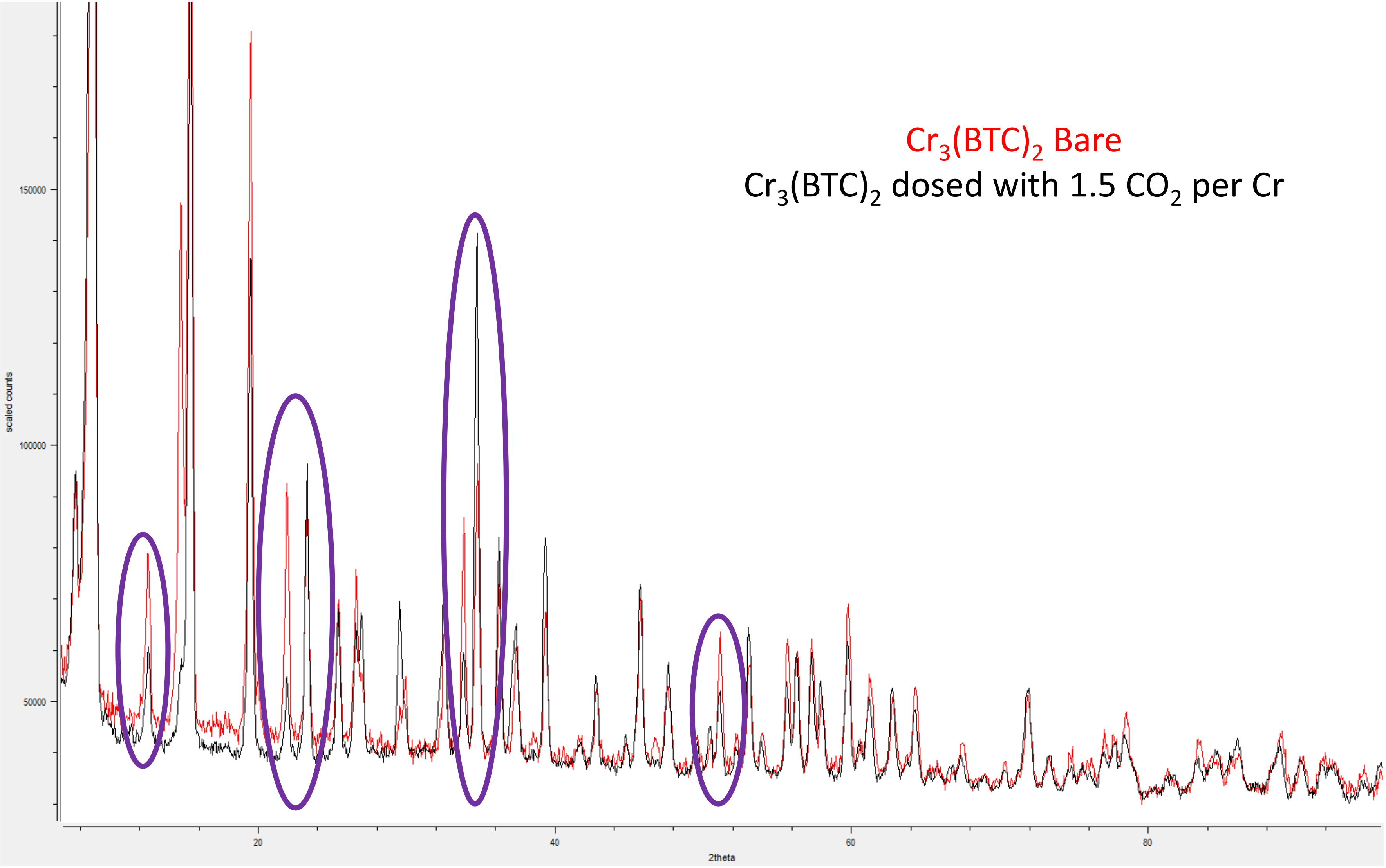
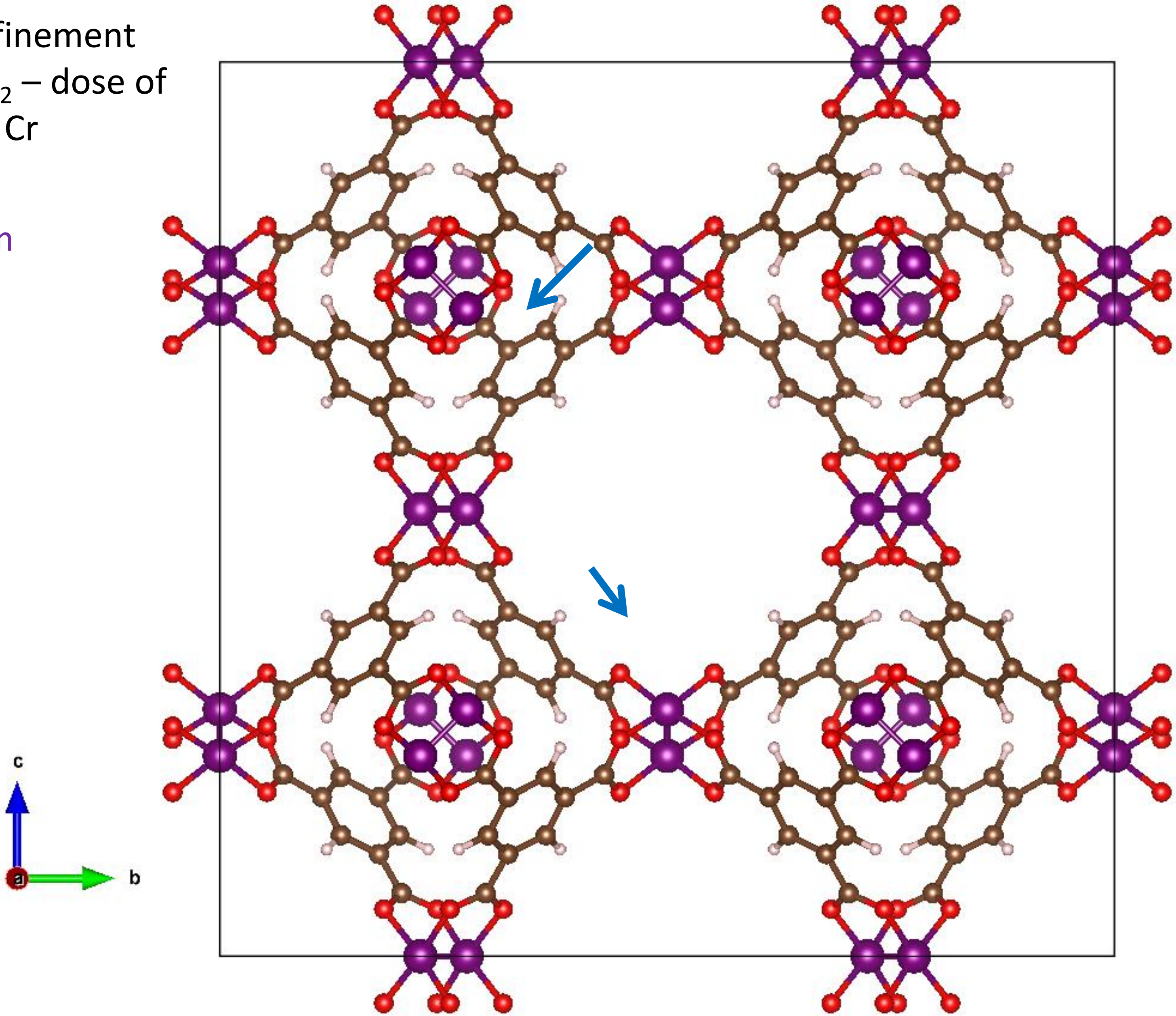
Neutron Powder Diffraction (cont.)



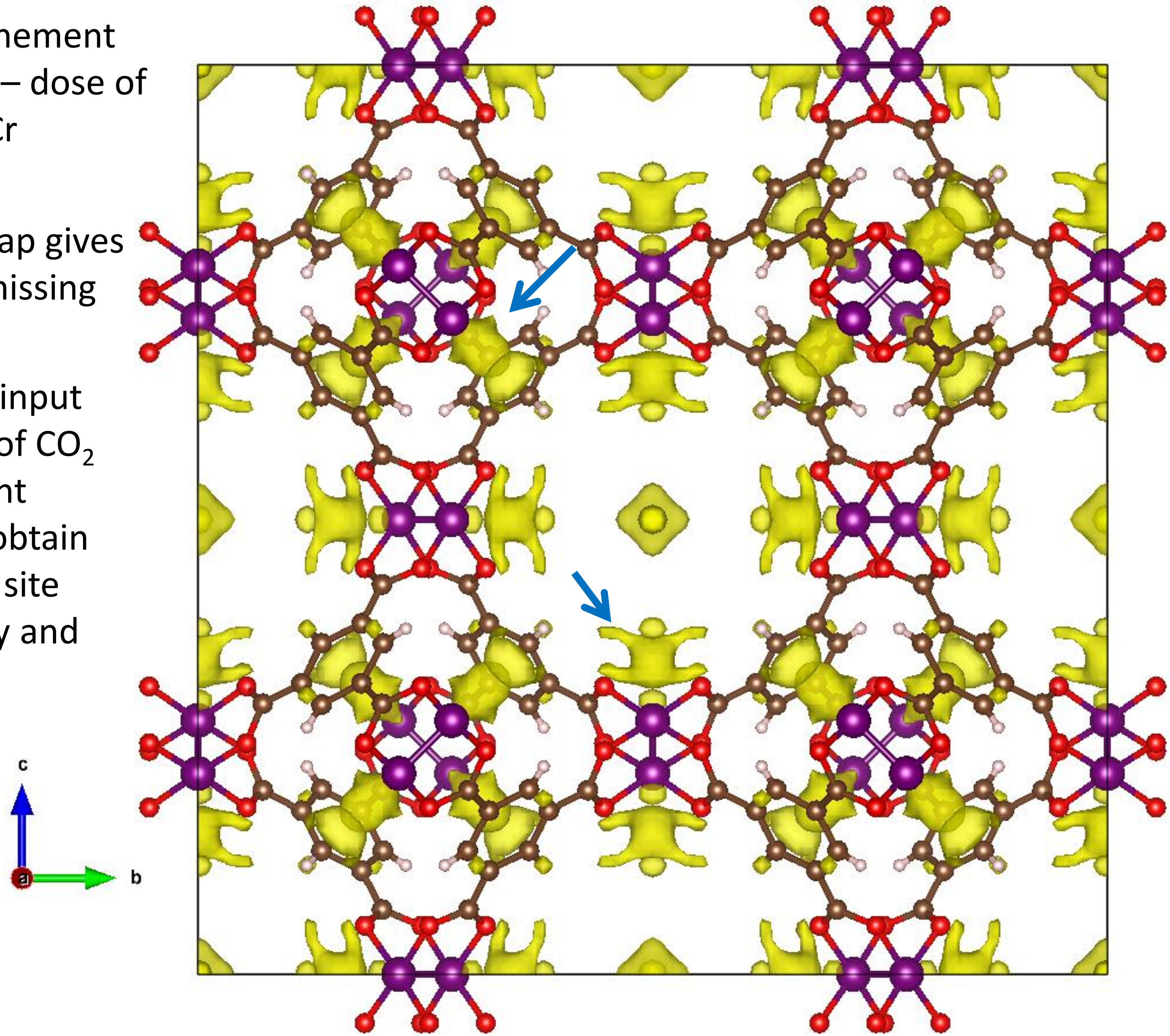
Rietveld Refinement for $Cr_3(BTC)_2$ – dose of 1.5 CO_2 per Cr

Chromium
Oxygen
Carbon
Hydrogen



Rietveld Refinement for $Cr_3(BTC)_2$ – dose of 1.5 CO_2 per Cr

- Fourier map gives areas of missing density
- Manually input locations of CO_2
- Refinement cycles to obtain best fit of site occupancy and location



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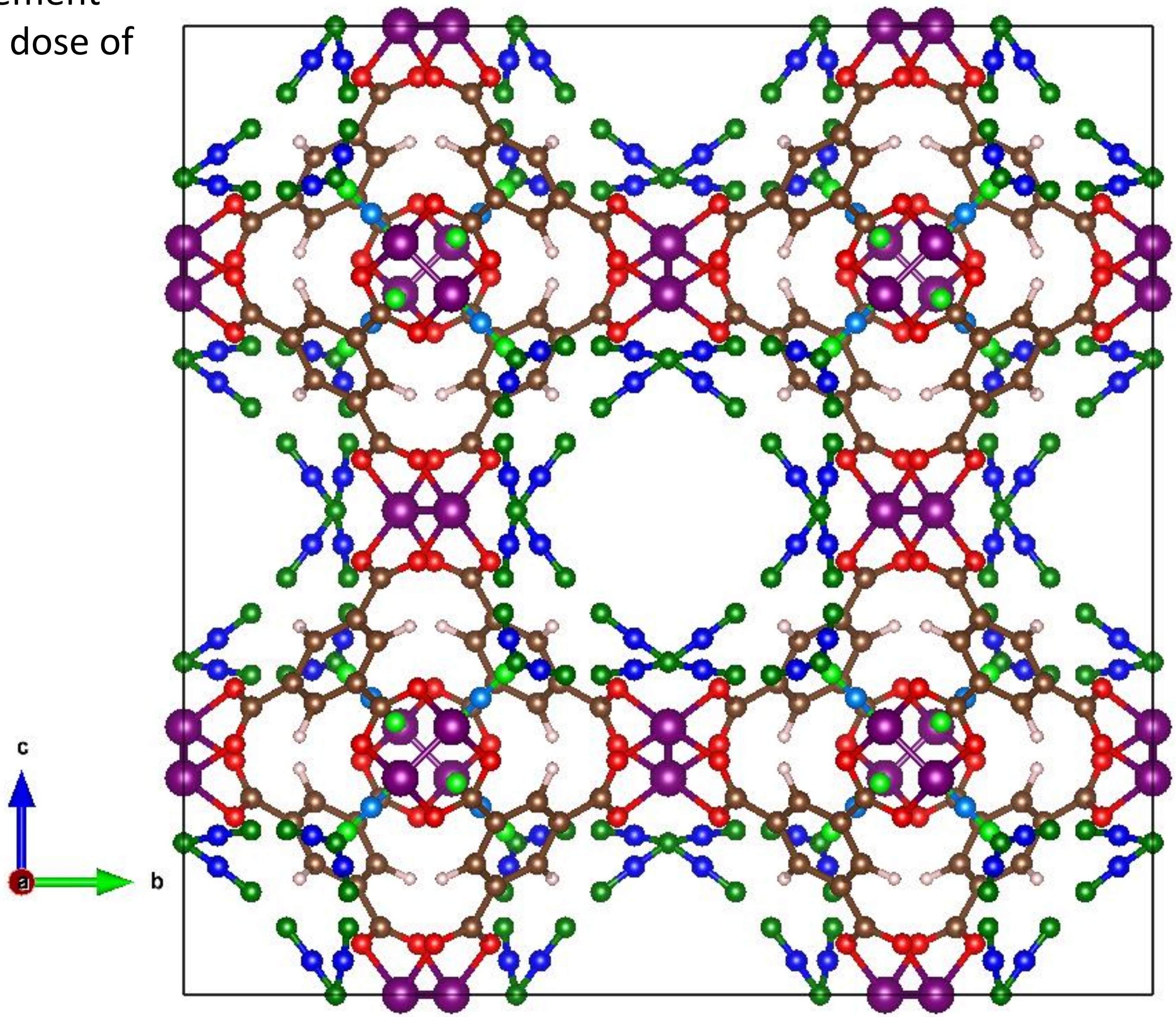

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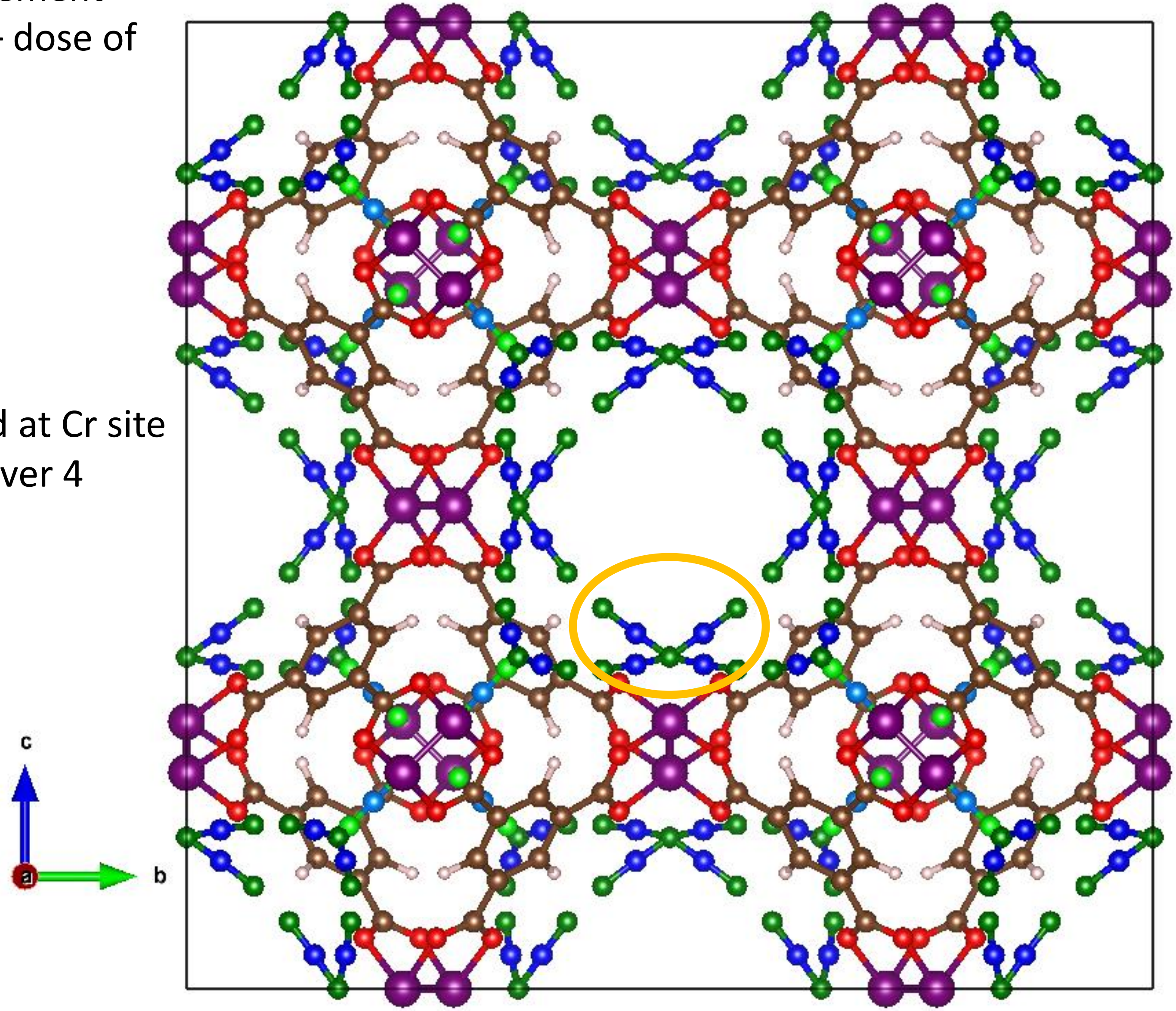

- CO_2 modeled at Cr site disordered over 4 orientations

Rietveld Refinement for $Cr_3(BTC)_2$ – dose of 1.5 CO_2 per Cr

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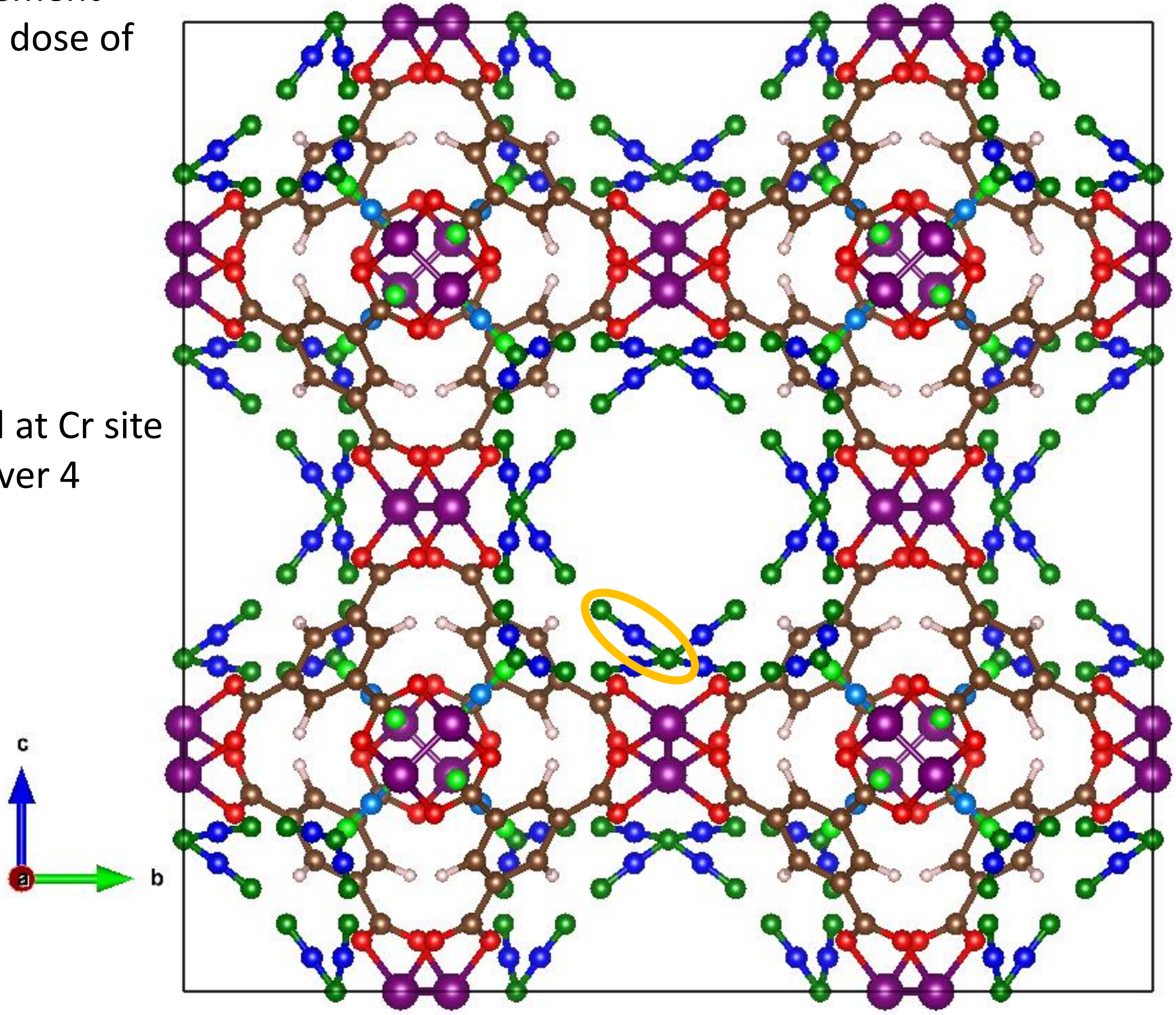

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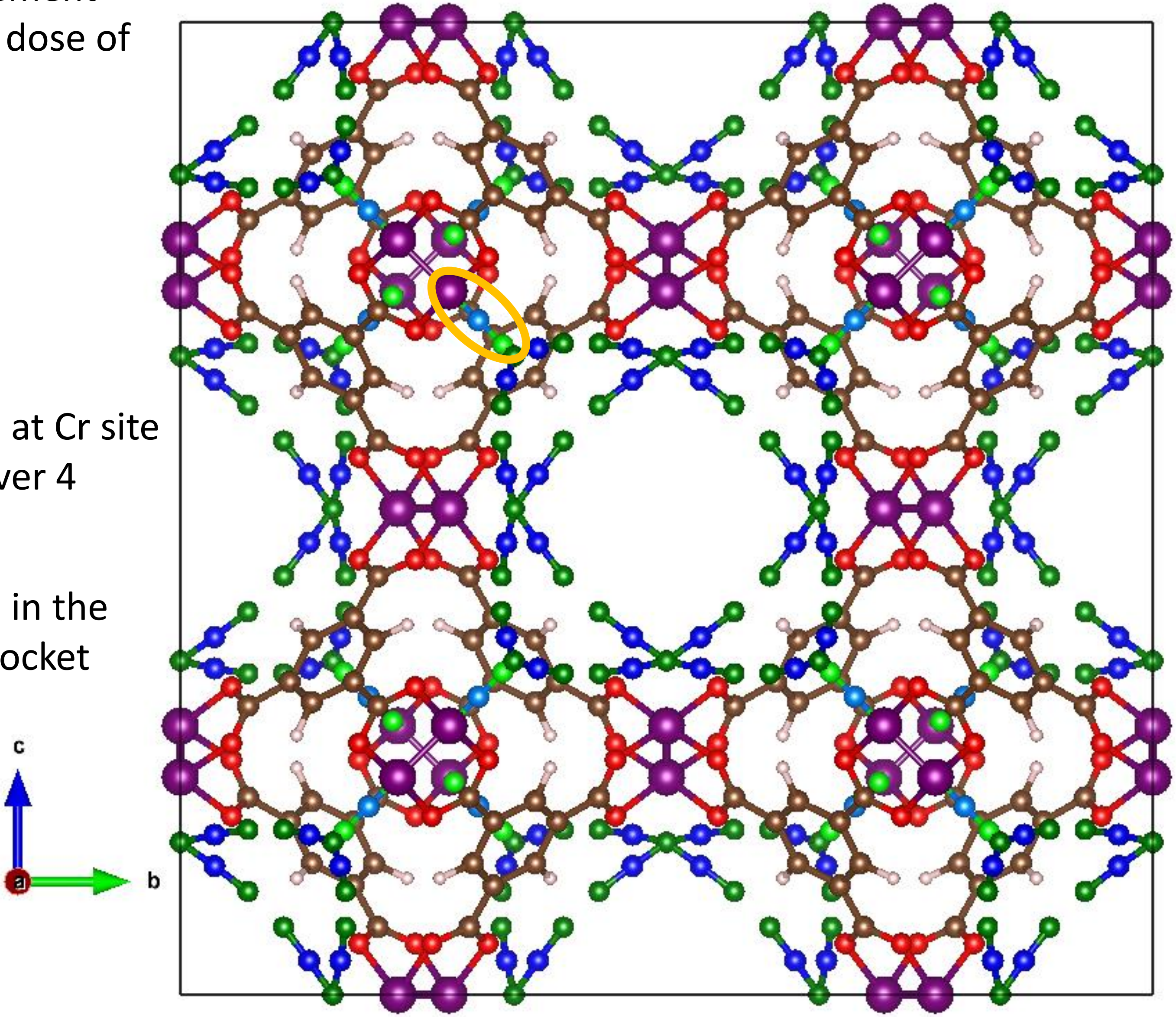
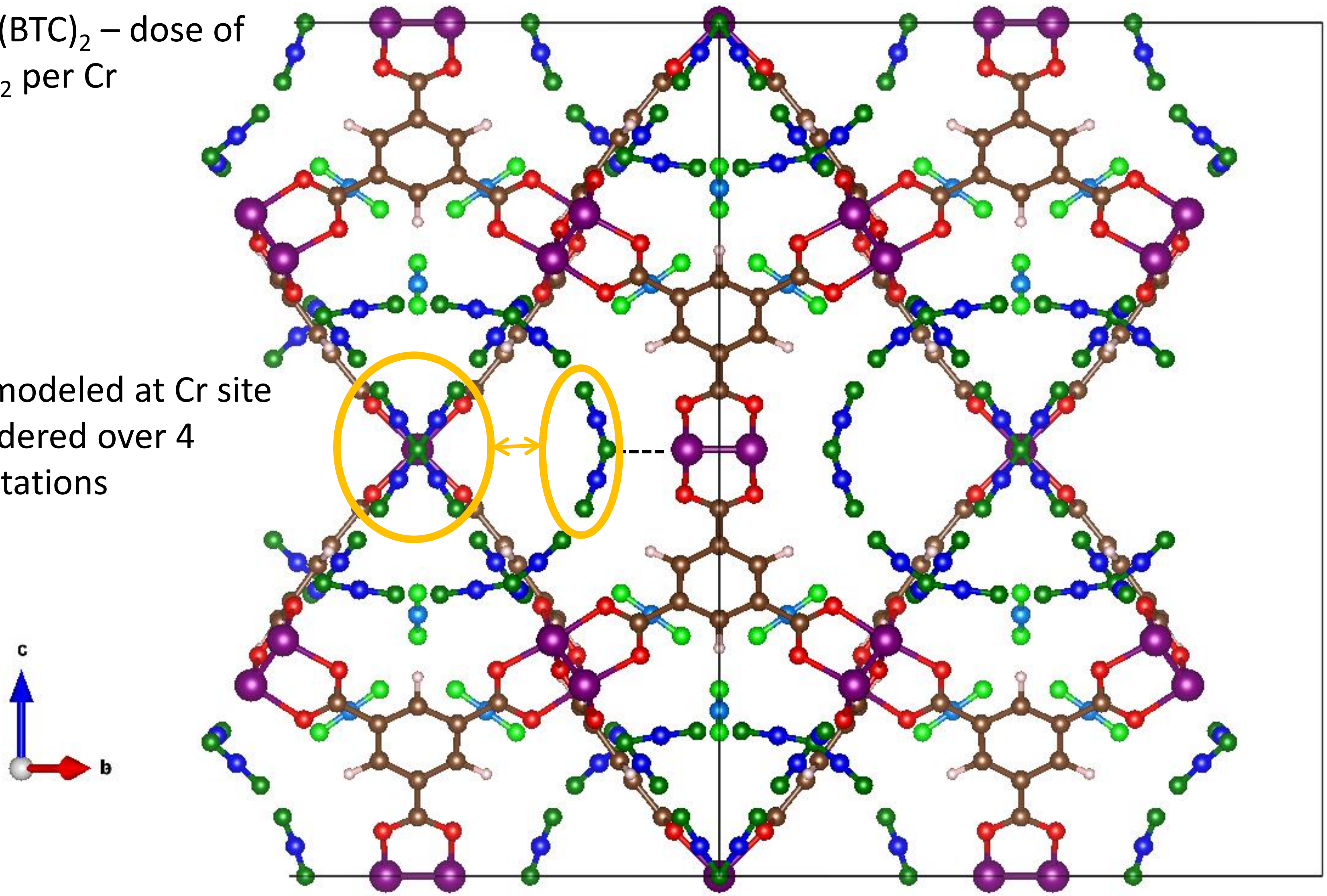


- CO_2 modeled at Cr site disordered over 4 orientations
- CO_2 modeled in the tetrahedral pocket

Rietveld Refinement for $Cr_3(BTC)_2$ – dose of 1.5 CO_2 per Cr

- CO_2 modeled at Cr site disordered over 4 orientations



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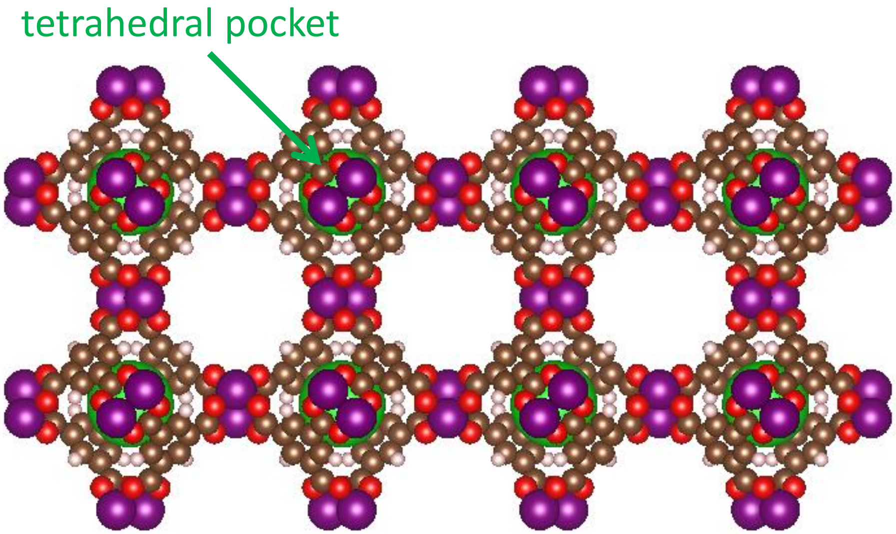
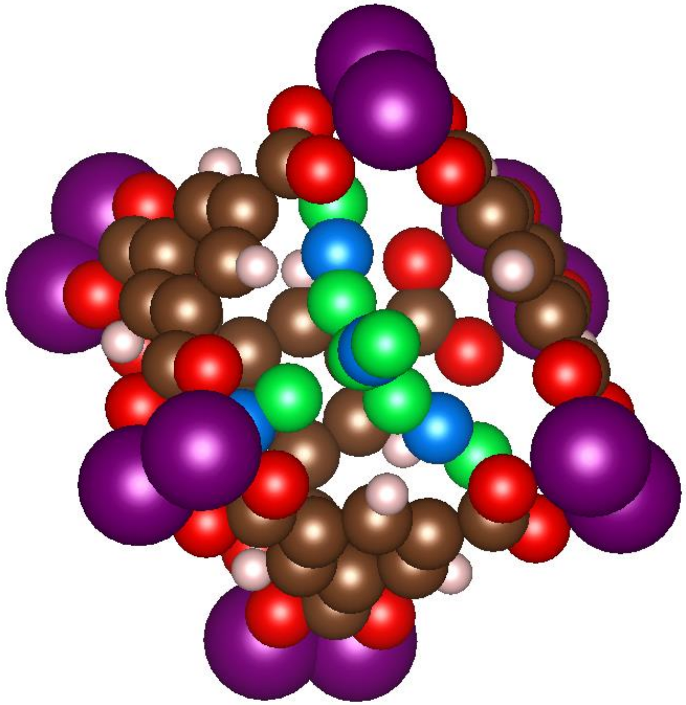
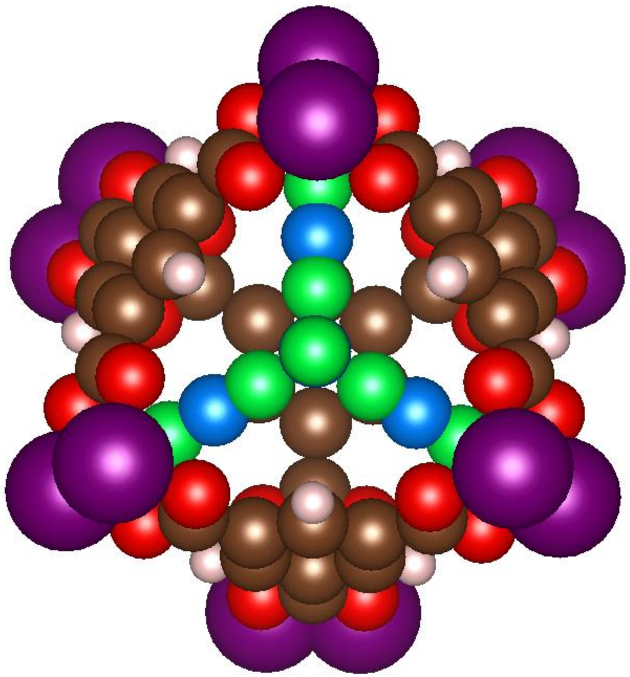
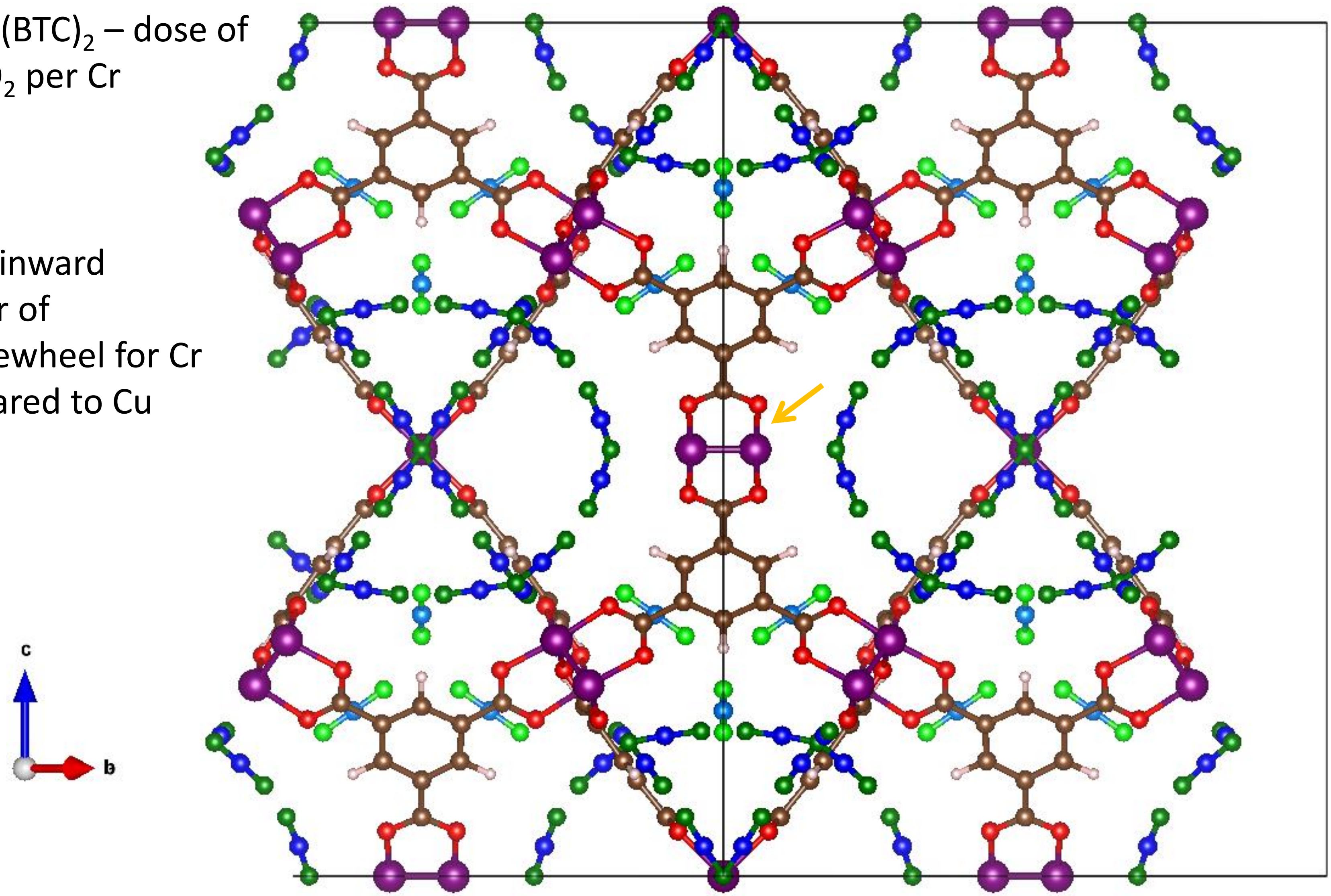






Reitveld Refinement for $Cr_3(BTC)_2$ – dose of 1.5 CO_2 per Cr

Slight inward pucker of paddlewheel for Cr compared to Cu



Comparison of $Cr_3(BTC)_2$ and $Cu_3(BTC)_2$

1.5 CO_2: $Cr_3(BTC)_2$

93 % metal sites occupied
68 % pocket occupied

1.0 CO_2: $Cu_3(BTC)_2$

42 % metal sites occupied
34 % pocket occupied

2.5 CO_2: $Cu_3(BTC)_2$

80 % metal sites occupied
70 % pocket occupied
23 % large pore site #1 occupied
14 % large pore site #2 occupied

Cr---OCO distance: ~ 2.58 Å
Cu---OCO distance: ~ 2.42 Å

Conclusions

- Primary CO_2 adsorption sites for both $Cr_3(BTC)_2$ and $Cu_3(BTC)_2$ found at:
  - unsaturated-metal center
  - inside tetrahedral pocket
- CO_2 displays slight preference towards metal site for both Cr and Cu, but both sites fill simultaneously
- Shorter interaction distance between CO_2 and unsaturated metal site for $Cu_3(BTC)_2$ over $Cr_3(BTC)_2$ due to pucker of Cr paddlewheel

Future Work

- More gas studies on $Cr_3(BTC)_2$
- Finish synthesis of $Mo_3(BTC)_2$
- Perform Neutron Diffraction Studies on $Mo_3(BTC)_2$

NIST Center for Neutron Research

Acknowledgements

- Special Thanks to:
  - Zeric Hulvey – NCNR/UMD
  - Rachel Pollock – NCNR/UMD
  - Efrain Rodriguez – UMD
  - Matt Hudson – NCNR
  - Craig Brown – NCNR
  - Julie Borchers – NCNR